

Nonlinear Regimes in Thermostats of Berendsen's Type

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Abstract

We consider the models of relaxational dynamics within the framework of Berendsen's and Nosé—Hoover's thermostats. On studying the crucial case of ideal gas we come to the conclusion that both models mentioned above do not allow for describing the true thermodynamical equilibrium.

1. Introduction

The thermodynamical concept of thermostat supposes that a system under consideration is a small part of a large system, or thermostat, which is big enough so as to be insensitive to changes inside the small one, and thus a very large number of particles is generally required to the effect. On the other hand, the small system may be in its turn rather tiny, even comprise only one particle. The thermostat's being macroscopical, creates serious difficulties for numerical modeling thermodynamical systems at fixed temperature and therefore, there is a need for simplified models that could accommodate the requirement of fixed temperature. The most straightforward approach to the problem is the use of the so-called collision thermostat, that provides adequate means for describing the system's interaction with ambient media. This method has its drawbacks in that it is time consuming and puts severe constraints on the precision level. Hence, it is very tentative to find certain simpler ways of modeling, using systems that do not involve extremely large number of particles or stochastic equations. The most familiar models in this respect are the Berendsen, [1] and the Nosé—Hoover, [2], one. The idea of both is the same: we shall introduce in the right hand sides of a system under consideration relaxation terms that contain a dissipation parameter that should mimic the control exercised on the system by thermostat. To this end one uses a relation, of the most simple form possible, that requires that the kinetic energy of the *total* system should be close to that prescribed by the heat energy determined by thermostat parameters. Thus, from the mathematical point of view, equations obtained in this way are an extension of the initial ones through the introduction of nonlinear dissipative terms in the right hand side. The prescription is quite general, appealing intuitively, and easy to implement. But it reduces the problem to that of a finite nonlinear dissipative system, with no macroscopical features left and essential thermodynamical properties being muted. Cosequently, one may wonder as to whether the physical nature of the phenomenon has been preserved.

In this paper we are going to consider examples of applying the prescription to a simple, but extremely important, case of ideal gas. Its analysis brings us to the conclusion that the Berendsen and Nosé — Hoover systems allow for interesting nonlinear regimes, even for this simple case, but do not generate the system's thermodynamical equilibrium.

2. Mechanical model

Let us recall the construction of the thermostats mentioned above. We shall begin with the Berendsen one. Suppose we have a system of particles whose dynamics is governed by the Newton equations

$$m_i \ddot{\vec{r}}_i = -\frac{\partial}{\partial \vec{r}_i} U(r)$$

The presence of a thermostat at temperature T is claimed to be accommodated through the introduction of non-linear dissipative terms in the equations indicated above, that is

$$m_i \ddot{\vec{r}}_i = -\frac{\partial}{\partial \vec{r}_i} U(r) - \gamma \dot{\vec{r}}_i \quad (1)$$

with the dissipative coefficient γ being of the form

$$\gamma = \alpha \left[\frac{1}{3k_b T N} \sum_{i=1}^N m_i \dot{\vec{r}}_i^2 - 1 \right] \quad (2)$$

where N is the number of particles. Intuitively, it is "clear" that the model described above by equations (1), (2) should guarantee that the system be at temperature T , or at least its total kinetic energy be close to that value. The distribution of the kinetic energy per particle is not so clear. To be more precise equation (1) in the notations of paper [1] contains the kinetic energy in the denominator; but it is not important for what follows.

In the Nosé — Hoover thermostat the dissipative variable γ is treated on equal footing with other dynamical variables, and instead of the algebraic equation (2) they write the differential equation

$$\dot{\gamma} = \alpha \left[\frac{1}{3k_b T N} \sum_{i=1}^N m_i \dot{\vec{r}}_i^2 - 1 \right] \quad (3)$$

The system of equations (1) and (3) is also quite appealing intuitively and looks excellently physically motivated. Again, at first sight it seems that the kinetic energy should be close to the heat one, at least if the system is kept long enough in the regime, and again one may have certain doubts, from the very beginning, as to its distribution with respect to degrees of freedom.

2. Ideal gas

Let us consider an ensemble of N noninteracting identical particles of mass

$$m_i = m, \quad i = 1, 2, \dots, N$$

that is an ideal gas, in a thermostat. Consider first the Berendsen one. Then the equation 1 takes the form

$$m\ddot{\vec{r}}_i = -\gamma\dot{\vec{r}}_i \quad (4)$$

in which i takes the values $1, 2, \dots, N$. It is more convenient to use the momenta

$$\vec{p}_i = m\dot{\vec{r}}_i, \quad i = 1, 2, \dots, N$$

and cast equations (1) in the form

$$\dot{\vec{p}}_i = -\gamma\vec{p}_i \quad (5)$$

On multiplying equations in (5) with $\vec{p}_i, i = 1, 2, \dots, N$ and next taking their sum, we obtain the equation for the energy E

$$\frac{d}{dt}E = -2\alpha E \left(\frac{2E}{3k_bTN} - 1 \right) \quad (6)$$

In equilibrium the value of energy is fixed, and therefore, the right hand side of the equation given above be equal to zero, so that we obtain the two values: (1) $E = 0$, which is meaningless, and (2) $E = \frac{3}{2}k_bTN$, which is the right one. But the second requirement still remains, that is the existence of Maxwell's distribution for velocities of particles. Here we run across serious difficulties. The main point is that thermostat ought to bring the system to the equilibrium, even if its initial configuration is outside the latter. Let us consider an initial state of the gas that comprises two beams of particles, the first one comprising of N_1 particles, all of them having the same momentum \vec{P}_1 , and the second one of the remaining $N_2 = N - N_1$ particles, all having the momentum \vec{P}_2 , $\vec{P}_1 \neq \vec{P}_2$. It is to be noted that equations (5) and (2) are invariant with respect to permutations of the indices i , that is we may interchange the particles so that solutions to equations (5), (2), remain valid. This is a form of Gibbs' principle, that is particles of ideal gas being not distinguishable from each other. But the particles of the first beam have the same initial momenta, \vec{P}_1 , and therefore they are described by the same equation in which

$$\vec{p}_i = \vec{P}_1, \quad i = 1, 2, \dots, N_1$$

and the same is true for the particles of the second beam, in which

$$\vec{p}_i = \vec{P}_2, \quad i = N_1 + 1, N_1 + 2, \dots, N$$

Thus, we may write only two equations for the momenta \vec{P}_1, \vec{P}_2 instead of N equations (5), that is

$$\dot{\vec{P}}_\nu = -\alpha \left[\frac{N_1 P_1^2 + N_2 P_2^2}{3mk_b T N} - 1 \right] \vec{P}_\nu, \quad \nu = 1, 2 \quad (7)$$

From the last equation we infer that the locus of stationary states for a gas having an initial state consisting of two beams of N_1, N_2 of particles, respectfully, is the ellipse in plane P_1, P_2 , given by the equation

$$\frac{N_1}{3k_b T N} P_1^2 + \frac{N_2}{3k_b T N} P_2^2 = 1 \quad (8)$$

In Fig.1 we illustrate the specific case of ten particles, the first beam comprises 3 particle and the second one 7. The particles move on a straight line with the momenta P_1 and P_2 , respectfully. The states given by equation(8) are by no means equilibrium thermodynamical states.

Let us turn to the ideal gas in the Nosé — Hoover thermostat. On using momenta we may cast equations (1), (3) in the form

$$\begin{aligned} \dot{\vec{p}}_i &= -\gamma \vec{p}_i \\ \dot{\gamma} &= \alpha \left[\frac{1}{3mk_b T N} \sum_{i=1}^N \dot{\vec{p}}_i^2 - 1 \right] \end{aligned} \quad (9)$$

Consider again the two beams of N_1 and N_2 particles having initial momenta \vec{P}_1 and \vec{P}_2 , respectfully. Similarly to the situation considered above, we may write equations (9) in the form of three equations

$$\begin{aligned} \dot{\vec{P}}_\nu &= -\gamma \vec{P}_\nu, \quad \nu = 1, 2 \\ \dot{\gamma} &= \alpha \left[\frac{1}{3mk_b T N} (N_1 P_1^2 + N_2 P_2^2) - 1 \right] \end{aligned} \quad (10)$$

Equations (10) have stationary states given by the constraint

$$\gamma = 0$$

and equation(8). In this sense the Nosé — Hoover thermostat is similar to the Berendsen one; they are also similar in that the stationary states are not thermodynamical equilibria, as is illustrated in Fig.2. But it is worth noting that Nosé — Hoover's thermostat, at least for the case of ideal gas we have

been studying, does not allow for attractor regimes, and in this sense it is even farther from the real thermostat than Berendsen's one.

3. Conclusion

The example of ideal gas shows quite convincingly that neither the Berendsen nor the Nosé — Hoover thermostat can serve as a device for modeling thermodynamical equilibrium. One may suggest, of course, that for system more sophisticated than an ideal gas they still could function to the effect, just owing to the complexity of a system under consideration, certain models of macromolecules, for example.

All the same, it is worthwhile to note that the Berendsen model is an interesting example of nonlinear dissipative problem, and its dynamics is characterized by the presence of a set in its phase space that attracts trajectories, that is an attractor. The latter is determined by the condition given by kinetic theory

$$\sum_{i=1}^N \frac{\dot{p}_i^2}{2m} = \frac{3}{2} k_b T N$$

In fact, it has also a more subtle structure of preserving the beams of particles with equal momenta, as was discussed above. Thus, at equilibrium the states of the system lie on a sphere in phase space. If the equilibrium had been of thermodynamical nature, we should have had a distribution of momenta corresponding to the canonical ensemble at a temperature prescribed by the thermostat. Instead, we have the equation (8), which describes the values of momenta for beams of particles of the same momentum. Thus, there is no canonical ensemble in the mechanical thermostat, which resembles more nonlinear dissipative systems like the Brusselator, [4]. At any rate, the system arrives at a stable state, following its evolution in time.

In contrast, Nosé — Hoover's system for ideal gas does not have attractors, even though the set of its stationary solutions is stable (see Fig.2 and 3).

References

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FIGURE CAPTIONS

Fig.1

Ten one dimensional particles in the Berendsen thermostat. The set of initial conditions for the momenta P_1, P_2 of the two beams of 3 and 7 particles corresponds to the set of trajectories which indicate the descent of the beams on the stationary states belonging to the ellipse given by equation (8).

Fig.2

Ten one dimensional particles in the Nosé — Hoover thermostat. The horizontal axes are P_1, P_2 , the vertical one gives values of γ . The closed curves indicate oscillatory motion round the set of stationary states, which is stable. The partition of the system into two beams is preserved, so that no thermodynamical equilibrium is achieved.

Fig.3

Ten one dimensional particles in the Nosé — Hoover thermostat. The horizontal axes are P_1, P_2 , the vertical one gives values of γ . A large amplitude motion of the beam; no thermodynamical equilibrium.

Fig.1

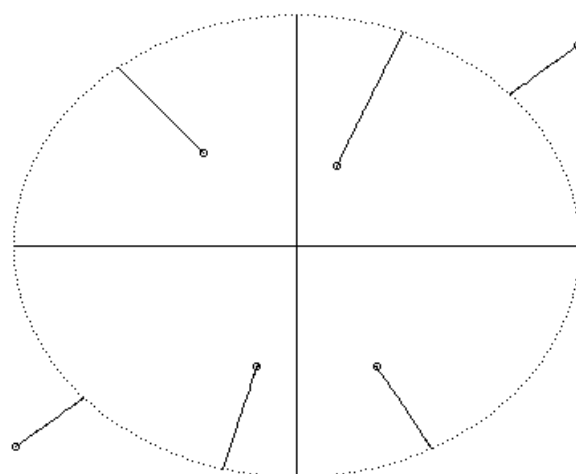


Fig.2

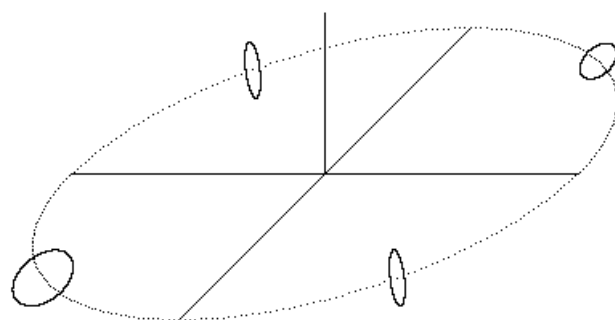


Fig.3

